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ACTIVE ACID CATALYST OF SULPHATED ZINC OXIDE FOR TRANSESTERIFICATION OF SOYBEAN OIL WITH METHANOL TO BIODIESEL

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Abstract: Active solid acid catalysts of sulphated zinc oxide (SO_4^{2-}-ZnO and SO_4^{2-}/ZnO) were prepared and characterized. The solid acid catalysts were investigated for their performance on transesterification of soybean oil with methanol to produce biodiesel. The SO_4^{2-}-ZnO and SO_4^{2-}/ZnO catalysts were prepared by coprecipitation and impregnation respectively to compare their performance for biodiesel production. The catalysts were characterized by X-ray Diffraction (XRD) and Fourier Transform Infra Red (FT-IR), while the fatty acid methyl ester (FAME) component in biodiesel product was identified by Gas Chromatography - Mass Spectrometer (GC-MS) and FT-IR. The SO_4^{2-}-ZnO catalyst, prepared by coprecipitation, showed better performance for the transesterification process than the SO_4^{2-}/ZnO catalyst, prepared by wet impregnation. The trend of performance of both catalyst was due to effect of sulfonate incorporation into the zinc oxide structure to form active acid sites. From the catalyst testing on transesterification of soybean oil with methanol at mild conditions (temperature of 65 ^oC, methanol to oil mole ratio of 6, and 4 wt% of catalyst loading), the SO_4^{2-}-ZnO catalyst exhibited promising FAME yield of 80.19% at 4 h reaction time. Therefore, the SO_4^{2-}-ZnO catalyst showed potential as a catalyst for transesterification of soybean oil to produce biodiesel.

Key words: sulphated zinc oxide; SO_4^{2-}-ZnO; soybean oil; transesterification; sulfonation

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1. Introduction

Current worldwide energy policies have been focused on development of sustainable renewable energy in order to reduce greenhouse gases due to fossil fuels usage. Related to this trend, biodiesel is an alternative fuel consisting of fatty acid methyl esters (FAME) produced by transesterification of triglycerides with methanol. The

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biodiesel is environmentally benign fuel due to biodegradable, nontoxic, low hazardeous emission, and renewable. The transesterification reaction could be catalyzed by homogeneous catalysts (alkalies and acids) or heterogeneous catalysts (solid acid or base). Until now, homogeneous base catalysts (KOH or NaOH) were well known used in industry, since this process has fast reaction rate at mild reaction conditions. Unfortunately, their utilization in vegetable oils transesterification has big problems due to forming soaps as undesirable byproducts, in which large amounts of wastewater was resulted, corrosiveness, and needs longer time for separation process.

Therefore, the use of heterogeneous catalysts allows a more environmentally benign process to be used for biodiesel production. The use of heterogeneous catalysts could enhance efficiency of reactor design, enable continuous process, and improve the economics of biodiesel production. The use of heterogeneous catalysts do not produce soaps through free fatty acid neutralization, which simplifies the separation and purification processes. Due to the potential interest of heterogeneous catalyst usage, researches on the transesterification reaction using the solid catalysts for biodiesel production has increased over the past decade. Heterogeneous catalysts could overcome the mentioned problems of homogeneous catalysts usage.

Previous researchers, including base and acid solid, have investigated a variety of solid catalysts for biodiesel production. The solid base catalyst includes CaO-based oxides [1-4], zinc oxide-based catalysts [5-10], and zeolites and modified zeolites [11-17]. Heterogeneous solid acid catalysts have been used as an alternative to basic and enzyme catalysts, since they can be used in both transesterification and esterification reactions [18]. However, acid catalysts required high alcohol-to-oil molar ratios and catalyst concentrations to achieve satisfactory transesterification conversions. The solid acid catalysts included sulphated zirconia [18-25].

Among the heterogeneous base catalysts, CaO was the most studied and the great potential for biodiesel production due to its low price and desired activity. The physical-chemical characteristics of CaO-based oxides showed improvement of surface area and thermal stability. This is probably due to the great enhancement of oil diffusion into catalyst surface which has been changed to be hydrophobic. In terms of solid acid catalysts, sulphated zirconia showed good catalyst for transesterification of vegetable oils [18, 21-23, 25] due to its strong acid properties and high activity and selectivity for the esterification of fatty acids with a variety of alcohols. The calcium oxide- and sulphated zirconia - based catalysts showed the potential of being used as a recyclable catalyst after simple regeneration without any significant loss in activity. In another researches, the transition metal oxide of zinc oxide was reported as a cheap, stable, reusable, commercially available, environmentally benign catalyst, and used in many catalytic reactions [2, 5]. It was also widely used as catalyst support. The ZnO-based metal oxides also showed good basic solid catalyst when modified with alkaline or alkaline earth metals for the transesterification of vegetable oils [26-28]. The modified ZnO was reported as a good catalyst for the transesterification of rapeseed oil owing to its high activity and minimum weight loss in supercritical methanol [28]. However, only a few previous researchers focused on development of potential sulphated-ZnO as a solid acid catalyst. Therefore, sulphate modified-ZnO, either prepared by coprecipitation or impregnation method, needs to be more studied for optimizing biodiesel production by transesterification process of vegetable oil. The incorporation of sulphate ions are expected showing strong influence on the phase modification of zinc oxide from thermodynamically more stable monoclinic to the metastable tetragonal or hexagonal phase. The sulfation is also expected leading to acidity increasing which may be due to presence of SO_4^{2-} ions on the surface of ZnO and also due to the formation of tetragonal or hexagonal phase as well as the increase in Lewis acidity of zinc oxide due to calcinations.

The aim of this paper is to obtain active catalysts based on sulphated zinc oxide which is prepared by coprecipitation and/or impregnation for the transesterification of soybean oil with methanol at mild reaction conditions. For this purpose, a series of catalysts were prepared, characterized, and compared, i.e. SO_4^{2-}-ZnO, SO_4^{2-}/ZnO, commercial ZnO, and synthesized ZnO. These catalysts were characterized by XRD and FT-IR, while the biodiesel product was identified by GC-MS and FT-IR.

2. Materials and Methods

2.1. Materials

Soybean oil was purchased from the local market (Happy-Indofood) to be used as raw material of triglyceride, while methanol (Merck, 99.9%) were used as reactant of transesterification. In terms of catalyst preparation, $Zn(NO_3)_2.4H_2O$ (Merck, 98%) and $ZnSO_4.7H_2O$ (Merck, 99.5%) were used as precursor of zinc oxide, while H_2SO_4 (Merck, 95-97%) and NH_4OH (Merck, 25%) were used as catalyst pretreatment or sulphation.

2.2. Catalysts Preparation

For synthesis of SO_4^{2-}/ZnO, ZnO was prepared by calcining $ZnSO_4.7H_2O$ at 727 ^oC for 5 h in a muffle furnace (Ney Vulcan 3-550). Thus, the resulted ZnO powder was immersed while stirred in 2 M solution of H_2SO_4 for 6 h at room temperature (28 ^oC). The mixed wet solid was dried in an oven (Memmert) at 110 ^oC for overnight. The resulted solid was calcined at 300 ^oC for 3 h in the muffle furnace.

For synthesis of SO_4^{2-}-ZnO, 2 M solution of $Zn(NO_3)_2$ was prepared by dissolving $Zn(NO_3)_2.6H_2O$ in distilled water. After preparation of zinc nitrate solution, ammonium hydroxide was drop wise added to it from burette. The reaction mixture was continuously stirred in a magnetic stirrer at room temperature for 30 minute till complete precipitation (pH 10-12). The precipitate was washed with distilled water and then dried in the oven at 100 ^oC for overnight. The dried precipitate was crushed, milled, and then sieved to get uniform sized particles. After sieving, the dried precipitate ($Zn(OH)_2$) was immersed while stirred in 1 N H_2SO_4 solution for 2 h. The mixed solid was then dried in the oven at 100 ^oC for overnight. The resulted solid was calcined in the box furnace at 500 ^oC for 3 h. The calcined catalyst was crushed, milled, and then sieved to get uniform sized particles. Meanwhile, commercial ZnO (MERCK, 99%) and the synthesized ZnO from $ZnSO_4.7H_2O$ (synthesized ZnO) was used for comparison.

2.3. Catalysts Characterization

The X-ray diffraction (XRD) patterns of the catalysts were recorded on an X-ray diffractometer (PANalytical) operating under 40 KV and 40 mA with the scan rate of 2°/min. The diffractometer employing Cu-Kα radiation to generate diffraction patterns from powder crystalline samples at ambient temperature. The Cu-Kα radiation was generated at scanning angle (2θ) from 5^o to 90^o. The Fourier Transform Infra Red (FTIR) spectrum of the catalysts were recorded on a SHIMADZU instrument using the KBr pellet technique and Attenuated Total Reflectance (ATR) method. The infra red scanning was done at 298 K and wave range of 4000-400 cm^{-1} with 2 cm^{-1} resolution.

2.4. Catalysts Testing for Transesterification

The sulphated zinc oxide (SO_4^{2-}-ZnO and SO_4^{2-}/ZnO) were tested for transesterification of vegetable oil to biodiesel using methanol. The sulphated ZnO catalysts were also compared to the commercial ZnO as well as ZnO synthesized from zinc sulphate. The transesterification reaction was carried out as follows. A 250 ml mixed solution of methanol and soybean oil with methanol to soybean oil molar ratio of 6:1, and 4 wt% solid acid catalyst were fed into a 500 ml flask as a batch reactor equipped with thermocouple and magnetic stirrer. The reactants were stirred at 300 rpm and the heating was started and kept at temperature of 65 ^oC. The good stirring was purposed to maintain uniform temperature and suspension. After running the transesterification reaction for a desired duration, the heater was switched off and the reactor was allowed to cool down naturally. After cooling, the product was discharged out and filtered using filter paper to separate the solid catalyst from the mixture of biodiesel–glycerol. The resulted FAME biodiesel was characterized and identified using GC-MS (SHIMADZU) equipped with Agilent DB-1 column and helium as a gas carrier. Additionally, in order to confirm the identified fatty acid methyl ester by GC-MS, the biodiesel product was also characterized by FT-IR spectroscopy.

3. Results and Discussion

3.1. Catalyst Characterization

Following reaction is supposed to take place in the preparation of main ZnO catalyst:

$$Zn(NO_3)_{2\,(aq)} + 2NH_4OH_{\,(aq)} \rightarrow Zn(OH)_{2\,(s)} + 2NH_4NO_{3\,(aq)} \quad (1)$$

$$Zn(OH)_{2\,(s)} \rightarrow ZnO_{\,(s)} + H_2O_{\,(g)} \quad (2)$$

In step 1 (Equation 1), zinc nitrate gave precipitated zinc hydroxide and ammonium nitrate. After washing, drying, and calcination (step 2) of dried precipitate of zinc hydroxide, a solid zinc oxide was obtained. Therefore, the zinc oxide was wet-impregnated with aqueous sulfuric acid solution which resulted in sulphated zinc oxide (SO_4^{2-}-ZnO). In this research, four catalysts were compared, i.e. SO_4^{2-}/ZnO, SO_4^{2-}-ZnO, synthesized ZnO, and commercial ZnO.

Structure analysis of compounds in the studied catalysts was investigated by FT-IR spectroscopy as shown in Figure 1. A broad absorption peak in the range of 3500-3700 cm^{-1} is present in all figures which can be attributed to the characteristic absorption of hydroxyl groups (O-H) by OH stretching vibration [6, 27]. This broad peak of OH represents a large number of water was adsorbed in the catalyst surface. The commercial and the synthesized ZnO showed similar FT-IR peaks trend. This fact suggests that the preparation of synthesized zinc oxide from zinc nitrate was well prepared. Peaks at 1630 cm^{-1} is due to bending of water molecules [27]. The peaks in the range of 450-1000 cm^{-1} is due to the presence of Zn-O bond [29, 30] for four catalysts. Sharper peaks evidence in the commercial ZnO than the synthesized ZnO indicates that the commercial ZnO is better than by coprecipitation of zinc sulphate. Metal-oxygen bonding in metal oxide catalyst is important as active component of the catalyst. Modification of the catalyst by SO_4^{2-} promoter was expected to change the catalyst structure. The modification was able to generate acid sites in the catalyst (Figure 1). From Figures 1(iii) and 1(iv), peaks at 1230-1370 cm^{-1} was assigned to S=O bonding in SO_4^{2-} [10, 22], while two bands at 1041 and 1182 cm^{-1} in the solid acid was assigned to the SO_2 asymmetric and symmetric stretching modes, respectively [22, 31, 32]. It indicates that the covalently linked sulfonic acid group was formed on the catalyst surface. However, the evidence of N-H peak at coprecipitated ZnO (Figure 1(i)) shows that the catalyst after coprecipitation is not completely washed by water to remove unreacted ammonia. Regarding the role of acid sites of the catalyst, the strong Brönsted acid sites is evidence at 3650 cm^{-1} due to O-H stretching on the sites. This fact is associated to the simultaneous absence of disulfate species and evidence of molecular water [22]. The band at 1620 cm^{-1} is attributed to the C=O stretching mode of the –COOH groups [31]. Therefore, the following functional groups, –COOH, $–SO_3H$ and –OH, were found in the solid acid catalyst.

The X-ray Diffraction pattern of SO_4^{2-}/ZnO and SO_4^{2-}-ZnO catalysts are shown in Figures 2(a) and 2(b) respectively. The catalysts structure were also compared to the synthesized ZnO (prepared from zinc sulphate precursor) and the commercial ZnO as shown in Figures 2(c) and 2(d), respectively. With respect to the SO_4^{2-}-ZnO catalyst, Figure 2(b) shows existence of two phases of monoclinic $Zn_3O(SO_4)_2$ (ICSD 01-071-2475) and hexagonal ZnO (ICSD 01-076-0704), in which the main phases are shown by $Zn_3O(SO_4)_2$ for 72 wt% followed by ZnO for 28 wt%. Meanwhile, 95 wt% monoclinic phase of gunningite ($Zn(SO_4).H_2O$ (ICSD 01-081-0022) and 5 wt% hexagonal ZnO (ICSD 01-079-0208) was detected in SO_4^{2-}/ZnO catalyst as shown in Figure 2(a). It is suggested that the SO_4^{2-}-ZnO catalyst has better structure and phase than the SO_4^{2-}/ZnO catalyst. Meanwhile, crystallite size, crystal structure, and crystal cell volume of four catalysts is listed in Table 1.

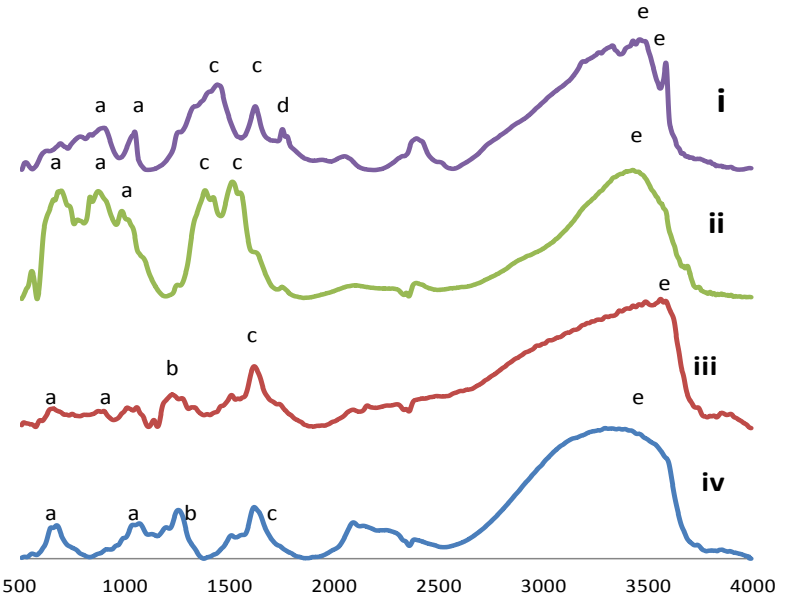

Fig. 1. FT-IR spectra for the catalysts: synthesized ZnO (i), commercial ZnO (ii), SO_4^{2-}/ZnO (iii), and SO_4^{2-}-ZnO (iv)

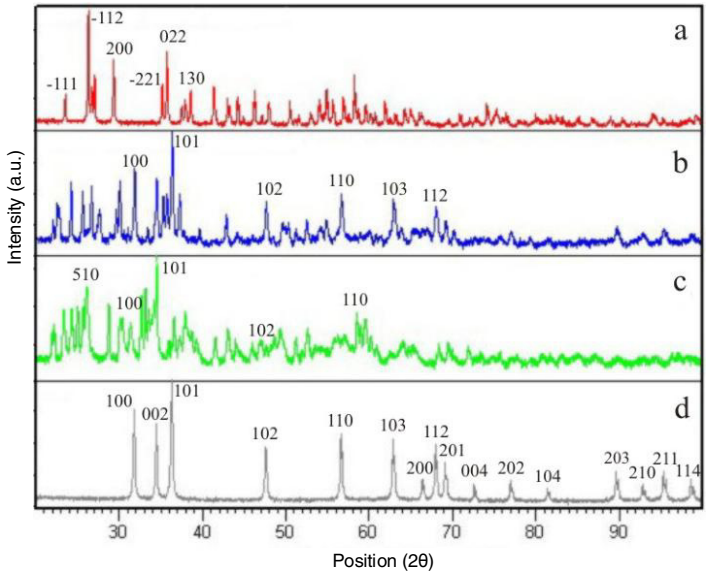

Fig. 2. The X-ray Diffraction pattern of the catalysts of SO_4^{2-}/ZnO (a), SO_4^{2-}-ZnO (b), synthesized ZnO (c), and commercial ZnO (d)

Table 1. Crystallite size of the catalysts using Scherrer equation

Catalysts	Crystal Structure	Crystallite size (nm)	Crystal cell volume (10^6 pm^3)
$SO4^{2-}$ - ZnO	monoclinic/hexagonal	15.908	344.01/47.77
$SO4^{2-}$/ ZnO	monoclinic	8.375	353.75
Commercial ZnO	hexagonal	14.361	47.61
Synthesized ZnO	monoclinic/hexagonal	8.368	709.2/48.18

According to the FT-IR and XRD analysis, it is observed that ZnO modified by sulphation was found to be an active catalyst for the transesterification of soybean oil with methanol which may be due to the creation of Brönsted acid sites as predicted in Figure 3 [5]. It was also reported that higher sulfur content corresponds to higher acidity of the catalyst and consequently higher catalytic activity [33].

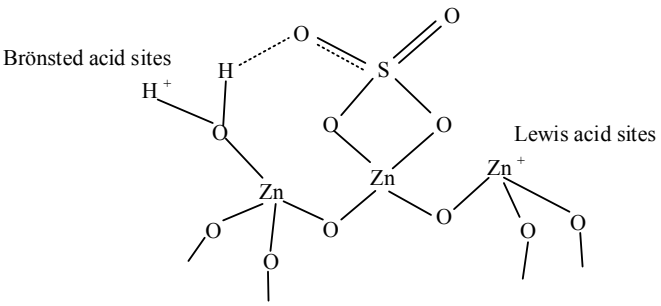

Fig. 3. Predicted structure of the Brönsted and Lewis acid sites on the sulphated zinc oxide

3.2. Catalytic Activity for Transesterification of Soybean Oil to Biodiesel

The catalyst (SO_4^{2-}-ZnO) was tested for transesterification of soybean oil to produce fatty acid methyl ester at mild reaction conditions (65 ^oC and reaction time of 4 h). In this reaction testing, methanol to soybean oil molar ratio is 6:1, while weight ratio of catalyst to oil is 4%. Yield of biodiesel (FAME) from this reaction is 80.19 % which implies the potential of the SO_4^{2-}-ZnO acid catalyst for the transesterification process. Meanwhile, biodiesel yield of 75.5 % was resulted when using the SO_4^{2-}/ZnO catalyst at similar reaction conditions. Therefore, the SO_4^{2-}-ZnO catalyst showed higher biodiesel yield than the SO_4^{2-}/ZnO catalyst. That's mean, incorporation of sulphate group or sulfonation to generate Brönsted acid sites in the coprecipitated SO_4^{2-}-ZnO is better than by impregnation. The incorporation of sulphate group in the form of monoclinic $Zn_3O(SO_4)_2$ as detected in XRD results (Figure 2 and Table 1) is able to generate Brönsted acid sites and Lewis acid sites as predicted in Figure 3. Meanwhile, impregnation of sulphate on the ZnO (become SO_4^{2-}/ZnO) showed weak acid sites as the FAME yield is lower than that by coprecipitation. From the catalyst characterization, the presence of –COOH, $–SO_3H$ and –OH functional groups leads to the formation of Brönsted and Lewis acid sites as predicted in Figure 3. The higher sulfur content corresponds to higher acidity of the catalyst and consequently higher catalytic activity [5].

The catalyst surface should posses some hydrophobic character for promoting the preferential adsorption of oily hydrophobic species on the catalyst surface and also to avoid deactivation of catalyst sites by strong adsorption of polar by products like glycerol or water. A strategy for controlling the hydrophobicity of metal oxide is by sulfonation as studied in this research. The enhanced catalytic performance in the transesterification reaction was explained by improved accessibility of the active sites and the hydrophobic organic groups into the zinc oxide. The Lewis acid site favor the formation of electrophilic species, which determine the rate of desorption followed by the rate of the transesterification reaction [34]. However, stronger Lewis acid did not favor product desorption easily which in turn makes the transesterification reaction slow [5, 35].

3.3. Characterization of Biodiesel Product using FT-IR and GC-MS

Characteristics of the soybean oil as raw material and the biodiesel product are specified in Table 2. It is shown that the biodiesel product is fulfil the requirement of SNI (Standard Nasional Indonesia) standard. Viscosity of the biodiesel product is within the range of standard, including density and acid value. Resulted biodiesel, mainly composed of fatty acid methyl esters, was analyzed using GC-MS to identify compound contents of the resulted biodiesel. To confirm the structural FAME content of the resulted biodiesel, a FT-IR spectroscopy was used to identify functional groups. The fatty acid methyl esters analysis identified by GC-MS is presented in Figure 4 and listed in Table 3. Main component of FAME product are 9,12-octadecadienoic acid methyl ester ($C_{19}H_{34}O_2$), 9-octadecenoic acid methyl ester ($C_{19}H_{38}O_2$), and eicosanoic acid methyl ester ($C_{21}H_{42}O_2$). The IR spectra of biodiesel product are also depicted in Figure 5 to confirm the GC-MS identification. From Figure 5, detected bands at 1099, 1121, 1163, and 1238 cm^{-1} were assigned to stretching mode of C-O, while appeared bands at 1400, 1377, 1418, and 1462 cm^{-1} were respected to bending mode of C-H. Stretching mode of C-H was also detected at bands of 2853 and 2924 cm^{-1}. With respect to C=O bonding in ester, the band at 1744 cm^{-1} was assigned to stretching mode of C=O. From the mentioned IR spectra, it is inferred that various groups composing fatty acid methyl esters are detected, i.e. alkana ($-CH_3$), ester (-COO-), and alkana (C-H).

Table 2. Characteristic of soybean oil raw and biodiesel product and the comparison to standard

Parameters	Soybean Oil	Biodiesel Product	SNI Standard
Density (gram/ml)	0.92	0.888	0.85-0.89
Kinematic viscosity (cSt)	15	5.73	2.3 – 6.0
Acid Number (%)	0.18	0.17	Max 0.8
Calorifc Value (cal/gram)	9320	9350	-

Table 3. GC-MS identification of biodiesel product from soybean oil

Peak Number	Compound Formula	Identified Chemical Compound	Composition (%)
1	$C_{10}H_{16}O$	2,4 Decadienal	11.45
2	$C_{10}H_{16}O$	2,4 Decadienal	22.18
3	$C_{14}H_{34}O_2SI_2$	Trimethylsilyl Ester	2.09
4	$C_{21}H_{42}O_2$	Hexadecanoic Acid Methyl Ester	4.28
5	$C_{21}H_{42}O_2$	Eicosanoic Acid Methyl Ester	9.73
6	$C_{19}H34O_2$	9,12- Octadecadienoic Acid Methyl Ester	28.72
7	$C_{19}H_{38}O_2$	9- Octadecenoic Acid Methyl Ester	19.37
8	$C_{19}H_{38}O_2$	Octadecanoic Acid Methyl Ester	2.18

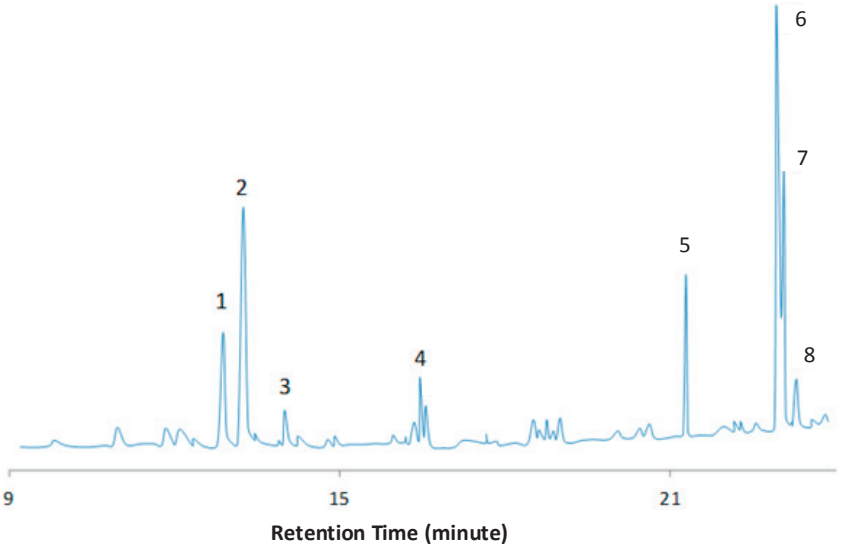

Fig. 4. GC-MS chromatogram of biodiesel product

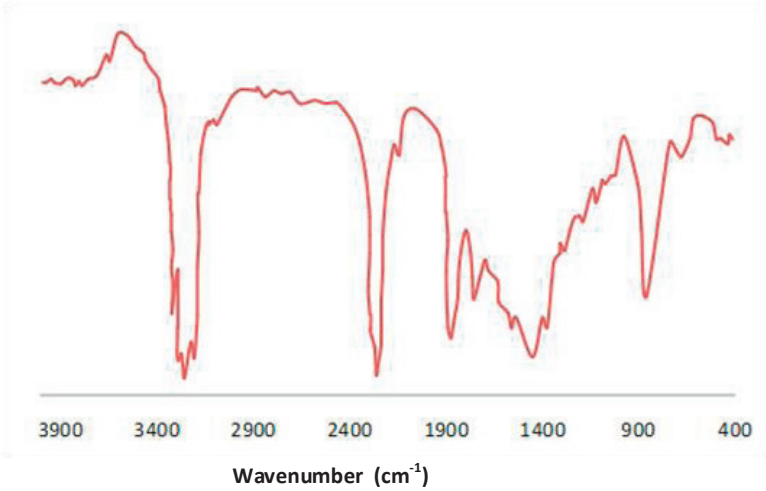

Fig. 5. FTIR characterization of biodiesel product

4. Conclusions

In this study, SO_4^{2-}-ZnO showed potential performance as catalyst for transesterification of soybean oil to fatty acid methyl ester. The SO_4^{2-}-ZnO exhibited an active solid acid catalyst for the transesterification reaction which could be attributed to the presence of Brönsted/Lewis acid sites on the catalyst surface due to incorporation of sulfonate groups into the catalyst surface. From the catalyst testing for transesterification of soybean oil at mild conditions (temperature of 65 ^oC, methanol to oil molar ratio of 6, and 4 wt% of catalyst loading), the SO_4^{2-}-ZnO catalyst exhibited promising yield of fatty acid methyl esters of 80.19% at 4 h reaction time, better than that of SO_4^{2-}/ZnO catalyst which only showed 75.5% yield. However, next studies should be focused on proofing presence and strength of Brönsted/Lewis acid sites as well as stability usage of the catalyst for biodiesel production.

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References

[1]. Kouzu, M., Hidaka, J. (2012). Transesterification of vegetable oil into biodiesel catalyzed by CaO: A review. Fuel. **93**,1-12

[2]. Ngamcharussrivichai, C., Totarat, P., Bunyakiat, K. (2008). Ca and Zn mixed oxide as a heterogeneous base catalyst for transesterification of palm kernel oil. Applied Catalysis A: General. **341**, 77-85.

[3]. Taufiq-Yap, Y.H., Lee, H.V., Hussein, M.Z., Yunus, R. (2011). Calcium-based mixed oxide catalysts for methanolysis of Jatropha curcas oil to biodiesel. Biomass Bioenergy. **35**, 827-834.

[4]. Yu, X., Wen, Z., Li, H., Tu, S.T., Yan, J. (2011). Transesterification of Pistacia chinensis oil for biodiesel catalyzed by CaO–CeO_2 mixed oxides. Fuel. **90**, 1868-1874.

[5]. Islam, A., Taufiq-Yap, Y.H., Chu, C.M., Chan, E.S., Ravindra, P. (2013). Studies on design of heterogeneous catalysts for biodiesel production. Process Safety and Environmental Protection. **91**, 131-144.

[6]. Kesić, Ž., Lukić, I., Brkić, D., Rogan, J., Zdujić, M., Liu, H., et al. (2012). Mechanochemical preparation and characterization of CaO.ZnO used as catalyst for biodiesel synthesis. Applied Catalysis A General. **427-428**, 58-65.

[7]. Kesica, Z., Lukic, I., Zdujic, M., Liu, H., Skala, D. (2012). Mechanochemically Synthesized CaO ZnO Catalyst For Biodiesel Production. Procedia Engineering **42**, 1169-1178.

[8]. Kim, M., Lee, H., Yoo, S.J., Youn, Y.S., Shin, Y.H., Lee, Y.W. (2013). Simultaneous synthesis of biodiesel and zinc oxide nanoparticles using supercritical methanol. Fuel. **109**, 279-284

[9]. Lukić, I., Kesić, Ž., Maksimović, S., Zdujić, M., Liu, H., Krstić, J., et al. (2013). Kinetics of sunflower and used vegetable oil methanolysis catalyzed by CaO·ZnO. Fuel. **113**, 367-378

[10]. Madhuvilakku, R., Piraman, S. (2013). Biodiesel synthesis by TiO_2-ZnO mixed oxide nanocatalyst catalyzed palm oil transesterification process. Bioresource Technology. **150**, 55-59

[11]. Babajide, O., Musyoka, N., Petrik, L., Ameer, F. (2012). Novel zeolite Na-X synthesized from fly ash as a heterogeneous catalyst in biodiesel production. Catalysis Today. **190**, 54-60

[12]. Borges, L.D., Moura, N.N., Costa, A.A., Braga, P.R.S., Dias, J.A., Dias, S.C.L., Macedo, J.L., Ghesti, G.F. (2013). Investigation of biodiesel production by HUSY and Ce/HUSY zeolites: Influence of structural and acidity parameters. Applied Catalysis A: General. **450**, 114-119

[13]. Dang, T.H., Chen, B.H., Lee, D.J. (2013). Application of kaolin-based catalysts in biodiesel production via transesterification of vegetable oils in excess methanol. Bioresource Technology. **145**, 175-181

[14]. Kusuma, R.I., Hadinoto, J.P., Ayucitra, A., Soetaredjo, F.E., Ismadji, S. (2013). Natural zeolite from Pacitan Indonesia, as catalyst support for transesterification of palm oil. Applied Clay Science. **74**, 121-126

[15]. Macario, A., Giordano, G., Onida, B., Cocina, D., Tagarelli, A., Giuffrè, A.M. (2010). Biodiesel production process by homogeneous/heterogeneous catalytic system using an acid–base catalyst. Applied Catalysis A: General. **378**, 160-168

[16]. Rashtizadeh, E., Farzaneh, F., Ghandi, M. (2010). A comparative study of KOH loaded on double aluminosilicate layers, microporous and mesoporous materials as catalyst for biodiesel production via transesterification of soybean oil. Fuel. **89**, 3393-3398
[17]. Wu, H., Zhang, J., Wei, Q., Zheng, J., Zhang, J. (2013). Transesterification of soybean oil to biodiesel using zeolite supported CaO as strong base catalysts. Fuel Processing Technology. **109**, 13-18
[18]. Nandagopal, J., Subramanian, S. (2010). Synthesis of Biodiesel from Neem Oil using Sulfated Zirconia via Transesterification. Brazilian Journal of Chemical Engineering. **27**, 601-608
[19]. Lam, M.K., Lee, K.T. (2010). Accelerating transesterification reaction with biodiesel as co-solvent: A case study for solid acid sulfated tin oxide catalyst. Fuel. **89**, 3866-3870
[20]. Melero, J.A., Bautista, L.F., Morales, G., Iglesias, J., Sánchez-vázquez, R. (2010). Biodiesel production from crude palm oil using sulfonic acid-modified mesostructured catalysts. Chem. Eng. J. **161**, 323-331
[21]. Patel, A., Brahmkhatri, V., Singh, N. (2013). Biodiesel production by esterification of free fatty acid over sulfated zirconia. Renew. Renew. Energy. **51**, 227-233
[22]. Platero, E.E., Pe, M. (1996). FTIR Studies on the Acidity of Sulfated Zirconia Prepared by Thermolysis of Zirconium Sulfate. Journal of Catalysis. **162**, 268-276
[23]. Rattanaphra, D., Harvey, A., Penjit, S. (2010). Simultaneous Conversion of Triglyceride / Free Fatty Acid Mixtures into Biodiesel Using Sulfated Zirconia. Topics in Catalysis. **53**, 773-782
[24]. Rattanaphra, D., Harvey, A.P., Thanapimmetha, A., Srinophakun, P. (2012). Simultaneous transesterification and esterification for biodiesel production with and without a sulphated zirconia catalyst. Fuel. **97**, 467-475.
[25]. Reddy, B.M., Sreekanth, P.M., Lakshmanan, P. (2005). Sulfated zirconia as an efficient catalyst for organic synthesis and transformation reactions. Journal of Molecular Catalysis A: Chemical. **237**, 93-100
[26]. Moezzi, A., McDonagh, A.M., Cortie, M.B. (2012). Zinc oxide particles: Synthesis, properties and applications. Chemical Engineering Journal. **185-186**, 1-22
[27]. Srivastava, V., Gusain, D., Sharma, Y.C. (2013). Synthesis, characterization and application of zinc oxide nanoparticles (n-ZnO). Ceramic International. **39**, 9803-9808
[28]. Yoo, S.J., Lee, H.S., Veriansyah, B., Kim, J., Kim, J.D., Lee, Y.W. (2010). Synthesis of biodiesel from rapeseed oil using supercritical methanol with metal oxide catalysts. Bioresource Technology **101**, 8686-8689
[29]. Azam, A., Ahmed, F., Arshi, N., Chaman, M., Naqvi, A.H. (2009). Low temperature synthesis of ZnO nanoparticles using mechanochemical route : A green chemistry approach. International Journal of Theoretical Applied Science. **1**, 12-14
[30]. Parthasarathi, V., Thilagavathi, G. (2011). Synthesis and Characterization of Zinc oxide Nanoparticle and Its Application on Fabrics for Microbe Resistant Defence Clothing. International Journal of Pharmacy and Pharmaceutical Sciences. **3**, 392-398
[31]. Zeng, D., Liu, S., Gong, W., Wang, G., Qiu, J., Tian, Y. (2013). Acid properties of solid acid from petroleum coke by chemical activation and sulfonation. Catalysis Communication. **40**, 5-8
[32]. Zhao, E., Isaev, Y., Sklyarov, A., Fripiat, J.J. (1999). Acid centers in sulfated , phosphated and / or aluminated zirconias. Catalysis Letters. **60**, 173-181.
[33]. Kiss, A., Omota, F., Dimian, A.C., Rothenberg, G. (2013). The heterogeneous advantage: biodiesel by catalytic reactive distillation. Topics in Catalysis. **40**, 141-150
[34]. Di Serio, M., Tesser, R., Dimiccoli, M., Cammarota, F., Nastasi, M., Santacesaria, E. (2005). Synthesis of biodiesel via homogeneous Lewis acid catalyst. Journal of Molecular Catalysis A: Chemical. **239**, 111-115
[35]. Endalew, A.K., Kiros, Y., Zanzi, R. (2011). Inorganic heterogeneous catalysts for biodiesel production from vegetable oils. Biomass Bioenergy. **35**, 3787-3809